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Nucleophilic attack by bromide ions as a first step of conversion of Se(VI) to Se(IV)

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Abstract

Numerous commonly used analytical methods allow only determination of a total amount of selenium in a given sample. Electroanalytical methods as well as those based on hydride generation or on formation of piazselenol allow only determination of Se(IV). To determine Se(VI) by these procedures, present alone or in mixtures with Se(IV), it is first necessary to convert Se(VI) to Se(IV). Such conversion is effective in the presence of excess of halides in acidic media or by photoreduction. In the often used conversion of Se(VI) in the presence of chlorides or less frequently of that of bromides, it has been assumed that the halide ion acts as a reducing agent. Kinetic studies of conversion of Se(VI) in acidic solutions containing an excess of bromide ions indicated that the rate determining first step of the reaction with Se(VI) is a nucleophilic substitution of the $-OH_2^+$ group in the protonated form of H_2SeO_4 by bromide ions. For the overall reaction with rate $-d[Se(VI)]/dt = k_1[H^+][Br^-]^{1.15}[Se(IV)]$ the rate constant $1 \times 10^{-3}\ L^2\ mol^{-2}\ s^{-1}$ was found. The following formation of Se(IV) from the bromo derivative is a fast reaction probably resulting in elimination of HBrO.

Keywords: Polarography; Selenium(IV) and (VI); Bromides; Nucleophilic substitution

1. Introduction

Selenium is present as trace element in nature. At low level it is essential for fulfilling several important physiological functions, but at higher concentrations it can be toxic. Hence the availability of reliable analytical methods for determination of its concentration is important. As the physiological effects of various forms of selenium differ, determination of all forms in which selenium is present is of interest. In nature selenium can be present in oxidation states +4 and +6 and as organoselenium compounds. The latter are usually converted into inorganic forms during the preparation of the sample. Thus the main analytical problem is the determination of Se(IV) and Se(VI) in a mixture.

Some techniques, like graphite furnace atomic absorption spectrophotometry [1–4], plasma atomic emission spectrophotometry [5], inductively coupled atomic emission spectrophotometry or mass spectroscopy [4,6–12] determine only the total amount of the selenium present. To achieve speciation, a separation technique – usually a variant of chromatography – has to be applied prior to the main analytical procedure [4,5,9–12].

Some techniques, such as hydride generation atomic absorption spectrometry [2,3,13–17] or formation of piazselenol in reaction of selenium (IV) with aromatic diamino compounds, followed by a spectrophotometric [18], fluorometric [19,20] or gas chromatographic [21,22] analysis, allow determination of only selenium in the oxidation state +4.

Similarly, reduction currents obtained by polarography or voltammetry offer information only about the concentration of Se(IV), as species containing Se(VI) are in the available potential range electroinactive. The understanding of the nature of the electrode processes involved is a condition for the successful application of electroanalytical techniques. This condition is fulfilled for the electroreductions of Se(IV), as the role of mercury in these reductions has been reorganized early [23,24]. The role of pH on the electrode process has been reinterpreted [25]. The use of polarography and voltammetry in the determination of Se(IV) has recently been reviewed [26]. Hence

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only some recent applications of the sensitive cathodic stripping voltammetry are quoted here [27–32]. Just one application of electroanalytical procedures, claimed to enable determination of nanomolar quantities of Se(IV) [33–35] will be mentioned here. In the proposed procedure, Se(IV) is reduced by sulfurous acid to Se(0), which with $SO_3{}^{2-}$ yields an adduct—$SeSO_3{}^{2-}$. This species is electrochemically reduced to Se^{2-}. The resulting selenide ion is in the vicinity of the electrode surface reoxidized to $SeSO_3{}^{2-}$ by iodate in the presence of hydroxylamine at pH 10. This catalyzed reduction of $SeSO_3{}^{2-}$ is manifested by a high catalytic reduction peak at −0.6 V. The proposed sequence of processes involved has yet to be supported by experimental evidence.

To analyze mixtures containing both Se(IV) and Se(VI) using above-mentioned techniques capable to determine only Se(IV), it is necessary first to determine the concentration of Se(IV) in the analyzed sample, then convert Se(VI) quantitatively to Se(IV), determine the sum of concentrations of Se(IV) and Se(VI) and to obtain the concentration of Se(VI) from the difference of results of the two above described determinations.

The choice of the reagent enabling a complete conversion of Se(VI) and Se(IV) is limited by the following constrains.

Commonly used reducing agents, such as hydrazine and hydroxylamine reduce Se(VI) to Se(0) [36]. Formation of Se(0) has been observed also in the presence of KI and H_2S [19]. Sodium borohydride reduces Se(VI) and Se(IV) all the way to Se^{2-} [36,37]. Sulfur dioxide does not reduce Se(VI) but reduces Se(IV) to Se(0) [36]. Addition of hydrogen peroxide results in a partial reduction of Se(VI) to Se(IV) [36].

Attempts have been made to convert Se(VI) into Se(IV) using irradiation of the sample using UV-light from a mercury lamp. This has been carried out both as a homogeneous and a heterogeneous process. In the homogeneous process a solution of Se(VI) containing 0.03% hydrogen peroxide and 0.1 M HCl was irradiated for about 1 h. (Significantly, when the same approach was carried out using 0.1 M H_2SO_4 or 0.1 M $HClO_4$ no reduction was observed.) To achieve a 90% conversion, addition of glucose or maleic acid was necessary. In the presence of other organic compounds lower conversion was observed. It was concluded [29] that the “irradiation procedure is empirical and its physico-chemical rationale is unknown.”

In other experiments in homogeneous solution, in the absence of glucose or hydrogen peroxide, about 100% conversion of Se(VI) into Se(IV) has been reported [27], when the solution containing chloride ions from investigated seawater was irradiated for 4 h [27]. Alternatively, irradiation at pH 11.0 for 1 h was proposed [38].

Photoreduction of Se(VI) was also attempted in heterogeneous systems, particularly in the presence of TiO_2 or silver loaded TiO_2 in the presence of formic acid [39,40]. In the first step the reduction yielded only Se(0), but when Se(VI) was exhausted, some reduction of Se(0) to Se(-II) took place. Reduction of Se(VI) has also been observed in the presence of enzymes [41] and bacteria [42–46], but this reaction has not been used for analysis.

The conversion of Se(VI) to Se(IV) can be achieved in solutions acidified by hydrochloric or perchloric acid in the presence of varying concentration of chloride ions at temperatures between 90 °C and 100 °C over varying periods of time [28,32,34–36,47–49]. The separate roles of acidity and chloride ions on the degree of conversion and the optimum time-period were, nevertheless, not clearly established. Thus, for example, the 100% conversion in 6 M HCl took at 90 °C several hours to establish [36]. Alternatively, such conversion was reported to be achieved in 5.8 KBr at 100 °C [15] or in 0.1 M KBr in 1.3 M HCl at either 90 °C or at boiling pint under reflux [20].

In all these investigations it was assumed that the halide acts as a reducing agent. Attempts to offer an interpretation based on comparison of standard potentials (sometimes using doubtful data [20]) are doubtful, as their use assumes a reversibility of the oxidation–reduction process. The time-periods and temperature needed for establishing the conversion strongly indicated that the processes involved are controlled by kinetics rather than thermodynamics. The essential consequence of a simple oxidation–reduction process would be formation of equivalent amounts of molecular Cl_2 or Br_2. No such observation has been reported, even when the reaction mixture was kept under reflux.

In this communication we propose that the initial step of the conversion of Se(VI) to Se(IV) in the presence of halides is a nucleophilic substitution by a protonated OH groups by the halide in an acid catalyzed reaction.

2. Experimental

2.1. Apparatus

Current–voltage curves were recorded using a PAR Model 174A Polarographic Analyzer with drop-time control. The capillary electrode used had natural by drop-time 2 to 3 s with out-flow velocity of 2.9 mg s^{-1} at mercury pressure used. A Kalousek electrolytic cell in which the KCl solution was replaced by 4 M NaCl to prevent formation of KClO, with an CE reference electrode, separated by a liquid junction, was used in a three-electrode configuration. The counter-electrode consisted of a Pt-wire.

DC polarograms were recorded with a Linseis LY 1600 X–Y recorder (Selt, Germany) using controlled drop-time of 2 s at a scan rate of 5 mV/s, DP polarograms with $t_1 = 1$ s at the same scan rate and pulse amplitude of 50 mV.

2.2. Reagents

Perchloric, hydrochloric, sulfuric acid and sodium bromide were analytical reagent grade. 0.1 M standard solution of Se(VI) was prepared by dissolving SeO_2 in hot water. Dilute solutions of Se(IV) were prepared fresh daily. Solute of 4 M $NaClO_4$ was prepared in situ by titrating $HClO_4$ by NaOH.

2.3. Procedures

2.3.1. Conversion yield

In previous studies the conversion of Se(VI) to Se(IV) was achieved in solutions containing 4–6 M HCl after boiling for 15–60 min [28,30,34–36]. Japanese authors [20] carried out the

Table 1
Dependence of yields of Se(IV) formed in conversion of Se(VI) on composition of the reaction mixture at 80 °C

Reaction mixture	Time (min)	Conversion yield (%)
1.0 M HCl, 2.0 M HCl, 2.0 M KBr, 2.0 M KCl	30	0
0.5 M HCl, 1.33 M KBr	60	90
1.0 M HCl, 1.33 M KBr	30	100
2.0 M HCl, 1.33 M KBr	30	100
4.0 M HCl	30	76 ± 4
4.0 M HCl, 0.66 M KBr	30	100 ± 2

reaction in a reaction mixture containing 0.33 M KBr and 1.3 M HCl.

To demonstrate the role of acidity, nature and concentration of halide ion the role of the composition of the reaction mixture has been studied (Table 1) at 80 °C to minimize the role of evaporation. Yields of Se(IV) were determined by transforming samples of reaction mixture to a buffer pH 4.0 and recording DPP curves.

Six milliliters of reaction mixture contained 0.1 mM Se(VI) (initial concentration), kept for chosen time-periods (Table 1) at 80 °C. Reaction was stopped by neutralization using sodium hydroxide and solution volume adjusted to 25 mL.

Two millilitres of sample was transferred to the polarographic cell to which 8 mL of the BR-buffer pH 4.0 was added and after deaeration the *i*–E curve was recorded. Complete conversion yielded 5×10^{-6} M Se(IV). For determination of the degree of conversion, the concentration of Se(IV) in each sample was determined by standard addition and measuring peak currents at −0.63 V and −1.18 V.

Conversion of Se(VI) to Se(IV) was more effective in the presence of bromide ions, so following experiments were carried out only in solutions containing bromide ions. As iodides and sulfides are known [19] convert Se(VI) to Se(0), their use was not investigated.

2.3.2. Kinetic studies

Dependence of yields on composition of the reaction mixture (Table 1) indicated that the conversions depended not only on the nature of the halide, but also on acidity. As in mixtures of HCl and KBr competitive reactions with both halides took place, majority of kinetics studies were carried out in reaction mixtures in which the acidity was controlled by $HClO_4$. To prevent formation of slightly soluble $KClO_4$ at the liquid junction, NaBr was used as a source of bromide ions to achieve complete conversion in time-periods shorter than 240 min.

Reaction mixtures containing chosen concentrations of $HClO_4$ and NaBr and either 10 mM or more frequently 1 mM Se(VI) were kept at 78 °C, after selected time-intervals small samples were taken and transferred into a solution containing 0.1 M $HClO_4$ and 0.1 M NaBr. The dilution resulted in stopping the reaction and at the same time the solution served as a supporting electrolyte. After removal of oxygen, DC polarographic curves were recorded. Concentration of Se(IV) was determined using standard addition.

To evaluate the measured rate constant in the given reaction mixture, the limiting currents were measured in two potential ranges indicated above, namely between 0.0 V and −0.15 V and between −0.4 V and −0.6 V (see below). The current at complete conversion i_∞ was determined as well as currents after individual time intervals (i). The rate constant k_1 (s^{-1}) in the given reaction mixture was obtained from the slope of $\log(i_\infty - i) = f(t)$ plots for currents measured in both potential ranges.

3. Results and discussion

The great majority of past studies of conversion of Se(VI) to Se(IV) in the presence of halides [15,20,28,32,34–36,47–49] has been carried out in solutions acidified with hydrochloric acid. Only the degree of conversion was reported. In the introductory part of our investigation the dependence of yields of Se(IV) formed by such conversions on composition of the reaction mixture were determined in solutions acidified by hydrochloric acid (Table 1). These studies indicated that the yields of Se(IV) depend both on acidity and on the nature and concentration of the halide. In order to be able to follow independently the effect of acidity and of the concentration of the halide, all subsequent investigations were carried out in solutions acidified by perchloric acid, to which a salt of the halide was added. As conversions were higher in the presence of bromide ions than those in chloride solutions, attention was concentrated on reactions with bromides. As the reaction evidently did not result in establishment of an equilibrium, investigation of its kinetics seemed to be indicated for elucidation of the initial steps of the process involved.

So far, a single study [49] paid attention to following the kinetics of conversion of Se(VI) to Se(IV) in solutions of hydrochloric acid at 91 °C. It has been demonstrated that the formation of Se(IV) follows kinetics, first order in selenium. The rate constants were $5.3 \times 10^{-4}\,s^{-1}$ in 4 M HCl and $3.9 \times 10^{-3}\,s^{-1}$ in 6 M HCl. It was concluded that the rate of the reaction increases sharply with concentration of hydrochloric acid. No attempts have been made to determine the order with respect to H^+ and Cl^-, but increase in rate with an approximately fourth power of concentration of hydrochloric acid was postulated.

In our kinetic studies the formation of Se(IV) was followed in reaction mixtures containing varying concentrations of hydrochloric or perchloric acid and varying concentrations of bromide ions. For the kinetic studies temperature of 78 °C was chosen to limit the evaporation during the kinetic run. In the course of 2 h, which was the longest time-period during which the kinetics was studied, less than 4% evaporation occurred.

In kinetic studies, polarography was used as an analytical method for determination of Se(IV) formed in the course of the reaction. Limiting currents were measured in two potential ranges, between 0.0 V (SCE) and −0.15 V and between −0.4 V and −0.6 V. The current in the most positive potential range in the acidic media studied corresponds to a reduction of mercury ions formed in a nonfaradaic oxidation of metallic mercury by $H_3SeO_3^+$ at the electrode surface [26]. The limiting current at about −0.5 V is a composite current, which results by

Table 2
Rate constants (k_{obs}) for rates of conversion of Se(VI) in solutions of strong acids of comparable acidity 0.9 M NaBr, 1 mM Se(VI), $T = 78\,°C$

Acid	H_0	μ	$k_{obs} \times 10^5\ s^{-1}$	k_{obs}/[acid] $\times 10^5\ s^{-1}$
1.72 M H_2SO_4	−0.82	5.16	170	98.8
1.95 M $HClO_4$	−0.80	1.95	180	92.3
2.28 M HCl	−0.83	2.28	230	101.0
				97.4

subtraction of a two-electron anodic current (corresponding to a formation of mercury selenide formed with the product of the reduction of Se(IV), which takes placed in a six-electron cathodic process [23,24,26]:

$$H_3SeO_3{}^+ + 6e + 3H^+ \rightarrow Se^{2+} + 3H_2O \quad (1)$$

$$2Hg \rightleftharpoons Hg_2{}^{2+} + 2e \quad (2)$$

$$Hg_2{}^{2+} + Se^{2-} \rightleftharpoons Hg_2Se \quad (3)$$

$$H_3SeO_3{}^+ + 4e + 3H^+ \rightarrow Hg_2Se + 3H_2O \quad (4)$$

Both these limiting currents, at about −0.1 V and −0.5 V, are a linear function of concentration of Se(IV).

The increase in concentration of Se(IV) with time in all kinetic runs followed first order kinetics in selenium, up to at least 80% conversion. The rate constant (k_{obs}) for each kinetic run was obtained from the slope of plots of log $i = f(t)$, where i is the measured limiting current.

The effect of acidity on the value of the rate constant k_{obs} has been investigated first in solutions of various strong acids. For concentrations of kinetics in solution of strong acids, concentrations of these acids of comparable acidity function H_0 were chosen. For compared acids (Table 2) the ratio k_{obs}/[acid] is constant within experimental error of about ±6%. The value in 2.28 M HCl may be increased by contribution due to the reaction with chloride ions. This indicates that the rate of the conversion is little affected either by the nature of anions present as counterions or by the ionic strength which is considerably different in investigated solutions.

To demonstrate the reproducibility of the investigated kinetics, the rate constants of the conversion in the presence of bromide ions were determined in repetitive experiments. The results indicated (Table 3) that for currents measured at the same potential the values of rate constants were reproducible within the range usually encountered in kinetic studies. Furthermore, values of rate constants obtained by measuring currents in two different potential ranges agreed within acceptable experimental error.

Table 3
Reproducibility of role constants k_{obs} for the reaction of bromide ions with Se(VI) 2.34 M HCl ($H_0 = -0.85$), 0.99 M NaBr, 1 mM Se(VI), $T = 78\,°C$

Current measured at	$k_{obs} \times 10^5\ s^{-1}$	Average
0.0 V	1.9 2.0 3.0 2.3 2.7	$2.4 \times 10^{-5}\ s^{-1}$
−0.04	2.1 2.1 2.75 2.0 2.4	$2.25 \times 10^{-5}\ s^{-1}$

Table 4
Dependence of observed rate constant (k_{obs}) on concentration of perchloric acid at constant ion strength 0.9 M NaBr, 1.0 mM Se(VI), $T = 78\,°C$

Ionic strength[a]	$\mu = 2.0$		$\mu = 3.0$	
[$HClO_4$]	[$NaClO_3$]	k_{obs}[b] $\times 10^5\ s^{-1}$	[$NaClO_4$]	k_{obs}[b] $\times 10^5\ s^{-1}$
0.1	1.0	8.05	2.0	7.5
0.29	0.71	17.3	1.71	21.0
0.50	0.60	41	1.60	44
0.70	0.40	57.5	1.40	58
1.00	0.10	83	1.10	88
1.98	0.9	175	1.00	180

[a] Including 0.9 M NaBr.
[b] Average value in both potential ranges used.

Investigation of the role of acidity on the reaction rate was carried out in solutions containing a constant concentration of bromide ions and varying concentrations of perchloric acid. Most reliable results were obtained in solutions, where the ionic strength was kept constant – either at $\mu = 2.0$ or $\mu = 3.0$ – by additions of solutions of sodium perchlorate (Table 4). In such solutions the dependence of k_{obs} on concentration of perchloric acid was up to 2 M $HClO_4$ practically linear (Fig. 1) with a slope in the presence of 0.9 M NaBr of $8.5 \times 10^{-4}\ L\,mol^{-1}\,s^{-1}$. This indicates that the reaction is first order in hydrogen ions, and – as indicated above – it does not depend on the nature of the anion. Data obtained in solutions of perchloric acid in the absence of sodium perchlorate (Table 5) show much larger deviations from the linear plot with the slope in the presence of 0.9 M NaBr of $5.6 \times 10^{-4}\ L\,mol^{-1}\,s^{-1}$.

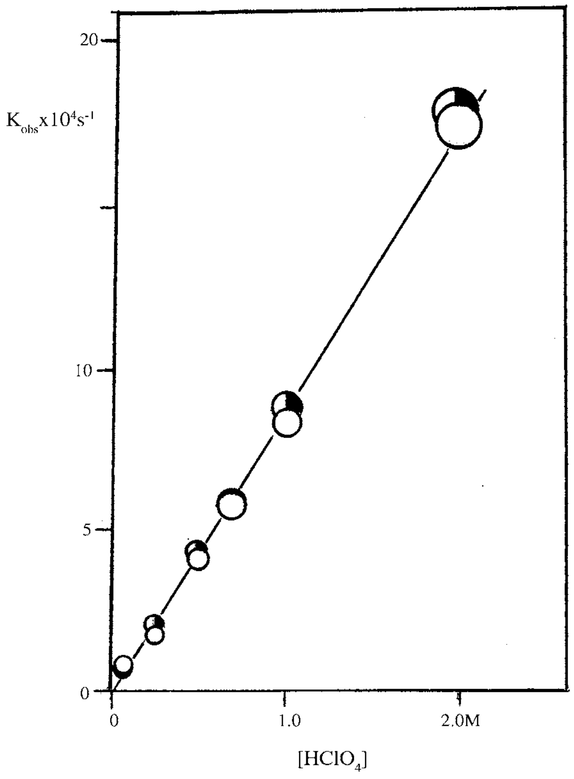


Fig. 1. Dependence of the observed rate constant k_{obs} on concentration of perchloric acid at constant ionic strength. Circles: $\mu = 2.0$; halved circles: $\mu = 3.0$. 0.9 M NaBr, 1.0 mM Se(VI), $T = 78\,°C$.

Table 5
Dependence of observed rate constants (k_{obs}) on concentration of perchloric acid at a varied ion strength 0.9 M NaBr, 10 mM Se(VI), $T = 78\,°C$, μ varied

[HClO$_4$]	$k_{obs}{}^{a} \times 10^5\ s^{-1}$
0.09	2.0; 2.8[b]
0.27	5.2; 4.8
0.45	27.0; 30.0[c]; 21.0
0.98	48; 68
1.98	180; 170

[a] Average values.
[b] 0.1 M HClO$_4$.
[c] 0.98 M NaBr.

Table 6
Dependence of the observed rate constant (k_{obs}) on initial concentration of bromide ions at ionic strength 3.0 0.99 M HClO$_4$, 1 mM Se(VI), $T = 78\,°C$

[Br$^-$]	[NaClO$_4$]	$k_{obs}{}^{a} \times 10^5\ s^{-1}$	log k_{obs}	log [Br$^-$]
0.1	1.90	8.05	−4.09	−1.0
0.3	1.70	18.75	−3.73	−0.52
0.5	1.50	39.0	−3.41	−0.30
0.69	1.30	50.5	−3.30	−0.16
0.99	1.00	105	−2.98	−0.004

[a] Average value.

Table 7
Dependence of the observed rate constant (k_{obs}) on initial concentration of bromide ions at varying ionic strength

[Br$^-$]	$k_{obs}{}^{a} \times 10^5\ s^{-1}$
0.01	0.68
0.1	6.3
0.5	23.0
1.0	59.0
2.0	22.0

[a] Average value.

In solutions containing about 1 M HClO$_4$ the observed rate constant k_{obs} increased with increasing concentration of bromide ions, both when the ionic strength was kept constant with addition of sodium percholate (Table 6) and when only the concentration of sodium bromide was varied (Table 7). But the increase in k_{obs} with bromide ion concentration was nonlinear (Fig. 2). To verify that these deviations from linear dependence on concentrations of Br$^-$ was not caused by a consecutive reaction involving the halide ion, the initial reaction rate v_0 was also measured at varying concentrations of bromide ions (Table 8). As opposed to rate constants the values of v_0 were more dependent on potential at which the current was measured. Nevertheless, initial rates obtained at both potentials have shown a nonlinear dependence on concentration of bromides (Fig. 3). Plots of log k_{obs} = f (n log[Br$^-$]) (Fig. 4) indicate an “n” value of about 1.15.

Table 8
Dependence of initial role (v^0, min^{-1}) on initial concentration of Br$^-$ ions in 1.0 M HClO$_4$, 1 mM Se(VI), $T = 78\,°C$, at varying ionic strength v^0 (min^{-1})^{a}

[Br$^-$]	Current measured	
	At −0.15 V	At −0.55 V
0.1	0.4	0.6
0.5	1.6	2.6
1.0	5.0	7.5
2.0	12.0	20.5

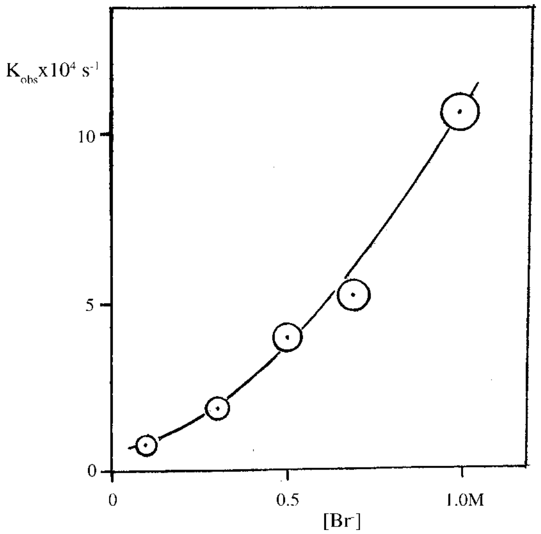


Fig. 2. Dependence of the observed rate constant k_{obs} on initial concentration of bromide ions at constant ionic strength; $\mu = 3.0$, 0.99 M HClO$_4$, 1.0 mM Se(VI), $T = 78\,°C$.

Thus the overall rate equation is

$$\frac{-d[\mathrm{Se(VI)}]}{dt} = k_1[\mathrm{H^+}][\mathrm{Br^-}]^{1.15}[\mathrm{Se(IV)}] \tag{5}$$

$$\text{and} \quad k_{obs} = k_1[\mathrm{H^+}][\mathrm{Br^-}]^{1.15} \tag{6}$$

From the slope of the dependence of k_{obs} on concentration of perchloric acid in the presence of 0.9 M NaBr (Fig. 2) which corresponds to $k_1[\mathrm{H^+}]$ it follows that $k_1 = k_{obs}/[\mathrm{H^+}][\mathrm{Br^-}]^{1.15} = 0.96 \times 10^{-3}\ \mathrm{L^2\,mol^{-2}\,s^{-1}}$. The value of k_1 can, nevertheless, be approached also from the dependence of log k_{obs} on log[Br$^-$] (Fig. 3). Extrapolating the plot of log k_{obs} on log[Br$^-$] to log[Br$^-$] = 0, the intercept yields in 1.0 M HClO$_4$ the value for $k_1 = 1.0 \times 10^{-3}\ \mathrm{L^2\,mol^{-2}\,s^{-1}}$, in good agreement with the result obtained from the dependence of k_{obs} on [H$^+$].

In some experiments transient yellow coloration of the reaction mixture was observed. Recording of UV–vis spectra recorded in a reaction mixture containing 1 M HClO$_4$ or 1 M H$_2$SO$_4$, 1 M NaBr and 1 mM Se(VI) as a function of time revealed formation of an intermediate, which absorbs at 390 nm. The maximum absorption at this wavelength rapidly increases with time, reaches a maximum value after about 30 s after mixing and then decreases. After 5 min no absorbance at 390 nm is observed. In the same reaction mixture a complete conversion of Se(VI) to Se(IV) is reached after about 60 min.

4. Mechanistic aspects

A simple oxidation–reduction process following the pattern (7) can be excluded

$$\mathrm{Se(VI)} + 2\mathrm{Br^-} \rightleftharpoons \mathrm{Se(IV)} + \mathrm{Br_2} \tag{7}$$

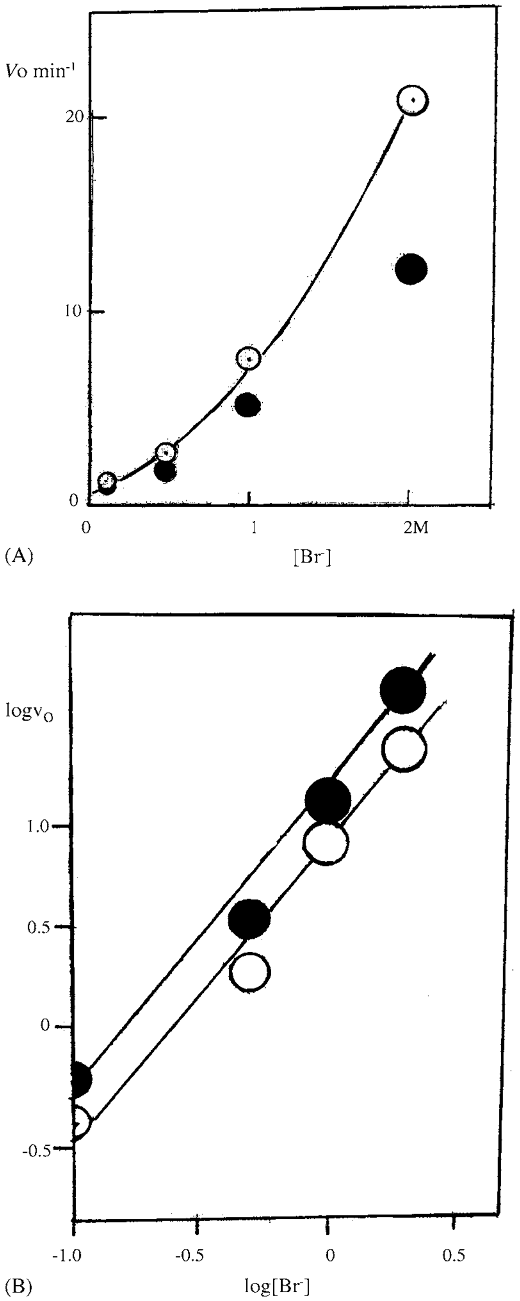


Fig. 3. Dependence of initial reaction rate v^0 (min^{-1}) on initial concentration of bromide ions at varying ionic strength; 1.0 M $HClO_4$, 1 mM Se(VI), $T = 78\,^{\circ}C$. Circles: current measured at −0.55 V; full circles: current measured at −0.15 V.

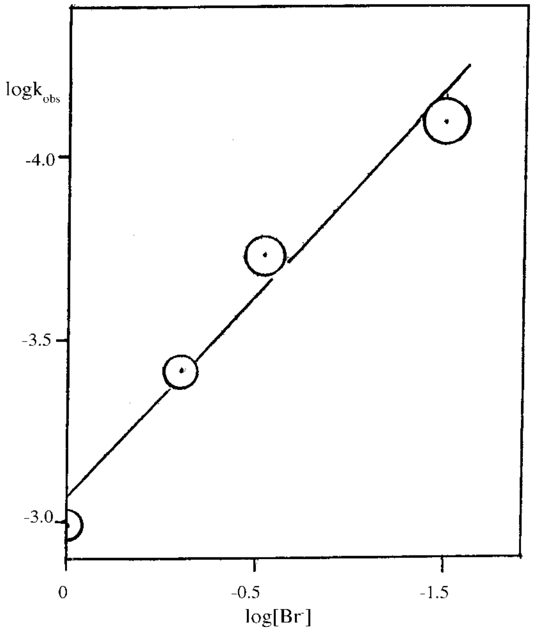
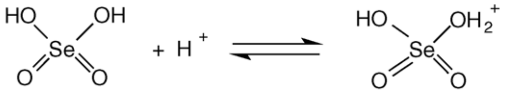


Fig. 4. Logarithm of rate constant k_{obs} as a function of logarithm of concentration of bromide ions. Conditions like in Fig. 2.

Neither polarography nor UV–vis spectra indicate formation of an equivalent amount of bromine. In spectra, recorded after a complete conversion of Se(VI) into Se(IV), no absorption corresponding to a bromine molecule was observed. Similarly, polarographic current–voltage curves recorded 10 min or longer after preparation of reaction mixture indicated absence of molecular bromine. As Br_2 is reduced at the DME at potentials more positive than that due to anodic dissolution of mercury, its presence is manifested by an increase of current at positive potentials. Nevertheless such increase of limiting current in the potential range between 0.0 V and −0.15 V has not been observed. Moreover, when during a kinetic run the change in current with time at 0.0 V and −0.55 V followed the same rate equation with the same rate constant. That would not be the case if Br_2 were present as the final product. Observation of transient absorbance at 390 nm may be attributed to a formation of bromine as a reactive intermediate, formed either in a consecutive process or in a side reaction.

Dependence of reaction rate on acidity and bromine concentration can be attributed to a nucleophilic attack of the bromide ion on protonated form of selenic acid (8), (9):



(8)

(I)

(9)

Species I then undergoes further reactions, following the overall process (10):

$$HSeO_3Br + H_2O \rightarrow H_2SeO_3 + Br^+OH^- \qquad (10)$$

The interpretation based on consideration as a nucleophile rather than a reducing agent is supported by the smaller reactivity of chloride ions. As the formation of Se(IV) is controlled by reaction (9) as the rate determining step, rate of reactions summarized in Eq. (10) must be faster than the rate of the sequence (8) and (9). As reaction (10) is faster than reaction (9), no direct evidence is available about the sequence of steps in process (10). Nonlinear dependence of k_{obs} on concentration of bromide ions may be due to participation of bromide ions in step (10).

The above observations and conclusions may be useful in a development of a more reliable procedure for determination of Se(VI) in mixtures with Se(IV).

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